

# High Temperature Aerogels for Thermal Protection Systems

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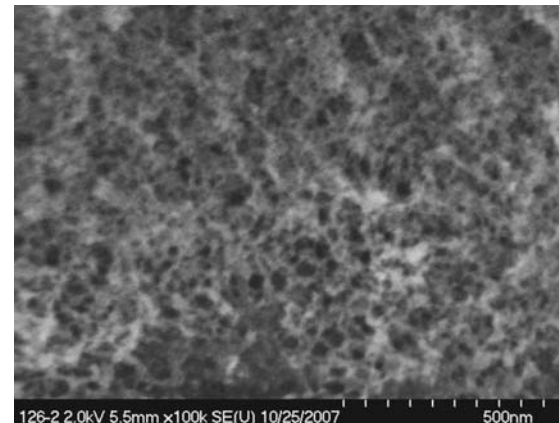
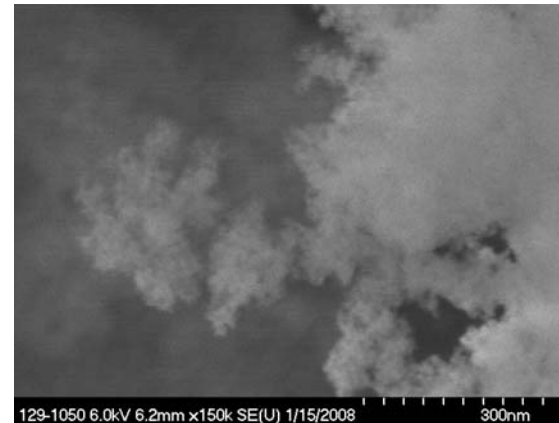
High temperature aerogels in the  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system are being investigated as possible constituents for lightweight integrated thermal protection system (TPS) designs for use in supersonic and hypersonic applications. Gels are synthesized from ethoxysilanes and  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , using an epoxide catalyst. The influence of Al:Si ratio, solvent, water to metal and water to alcohol ratios on aerogel composition, morphology, surface area, and pore size distribution were examined, and phase transformation on heat treatment characterized. Aerogels have been fabricated which maintain porous, fractal structures after brief exposures to 1000 C.

Incorporation of nanofibers, infiltration of aerogels into SiC foams, use of polymers for crosslinking the aerogels, or combinations of these, offer potential for toughening and integration of TPS with composite structure. Woven fabric composites having  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  aerogels as a matrix also have been fabricated. Continuing work is focused on reduction in shrinkage and optimization of thermal and physical properties.

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32nd Annual Conference on Composite Materials and Structures  
Daytona Beach, FL, January 28-31, 2008

## Acknowledgments:

Aeronautics Research Mission Directorate--Supersonics Project

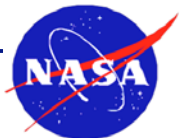
NASA Summer Faculty Fellowship Program

Janet B. Hurst, NASA GRC

Amy J. Tricamo, Ohio Third Frontier Program  
Applied Sciences, Inc.

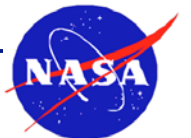
HyperTherm, Inc.

Anna Palczer, NASA GRC  
Dan Scheiman, ASRC  
Rick Rogers, NASA GRC  
Robert Mattingly, NASA GRC

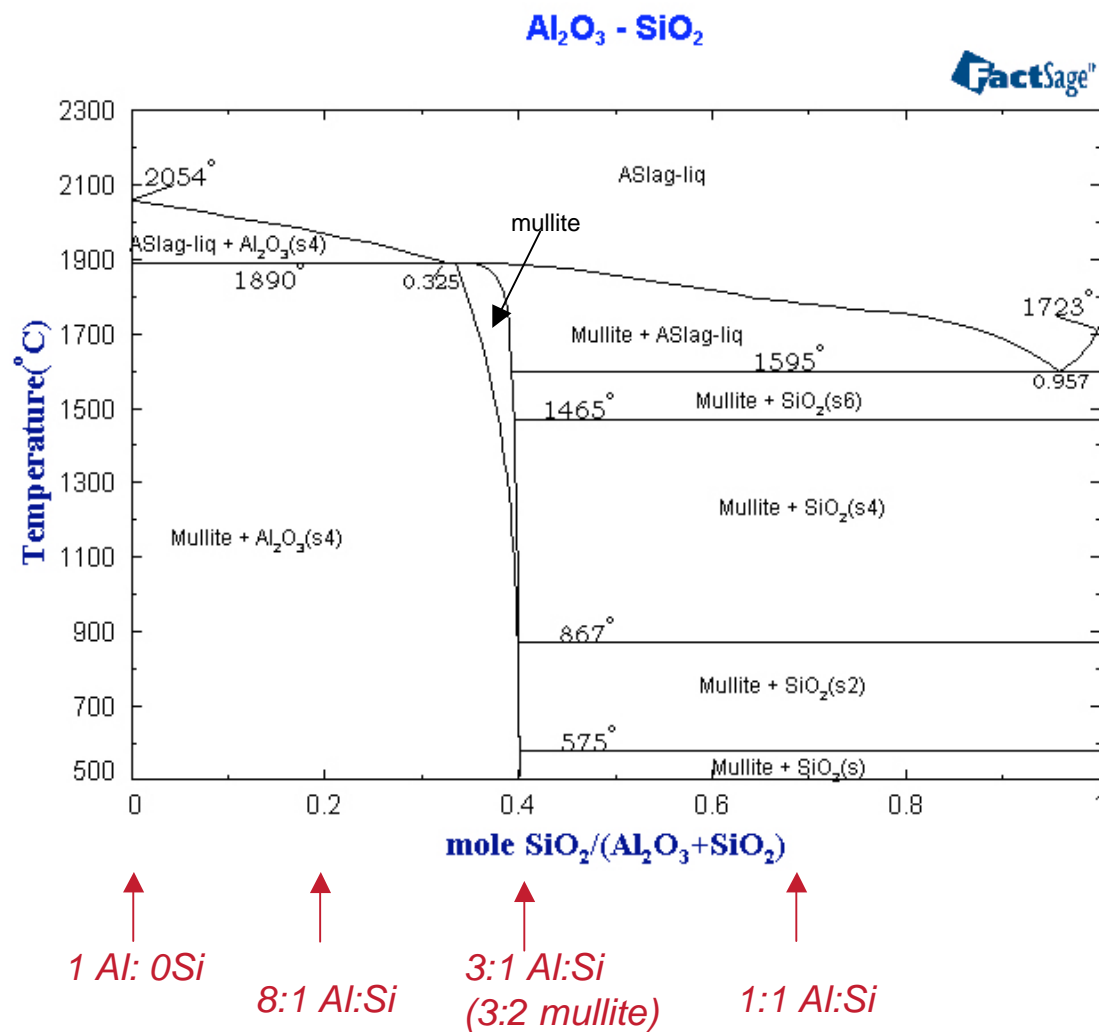


## Objective:

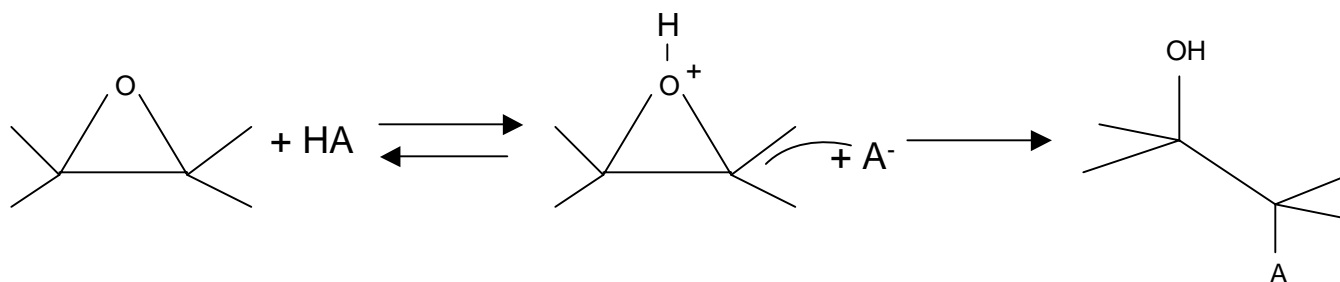
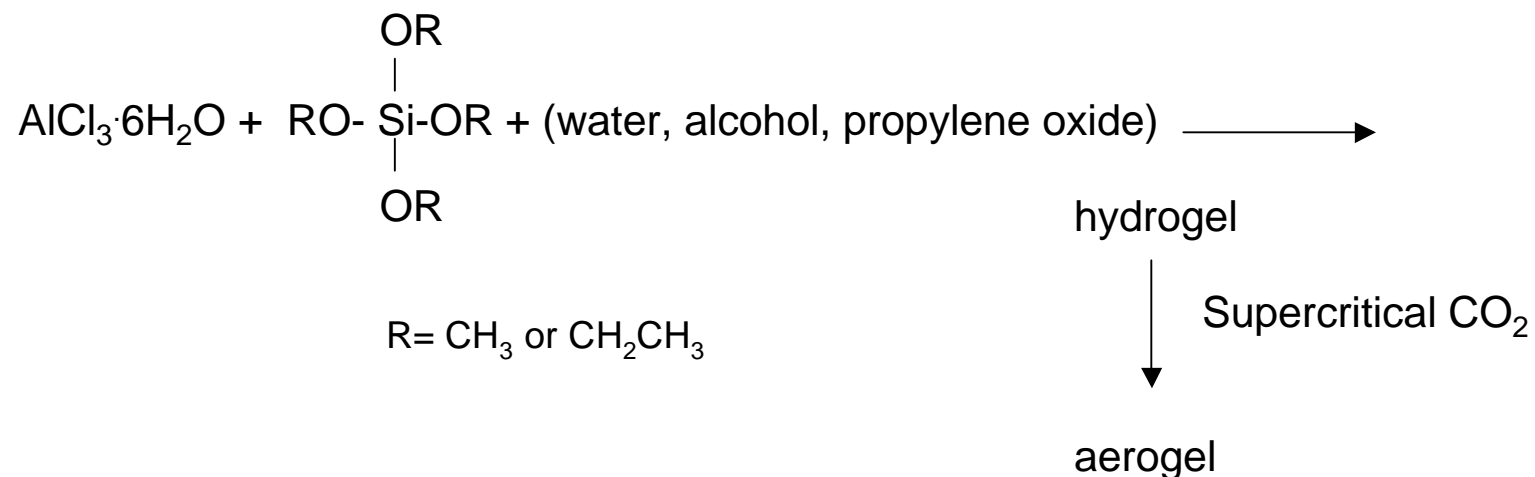
To explore the use of high temperature aerogels in the development of lightweight, high temperature insulating materials and integrated structures for supersonic and hypersonic applications, including space exploration.



## Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Phase Diagram-- Target compositions



## Synthesis approach:



- B. J. Clapsaddle, *et al.*, *J. Non-Crystalline Solids* **350**, 173-181 (2004)/

Variables:

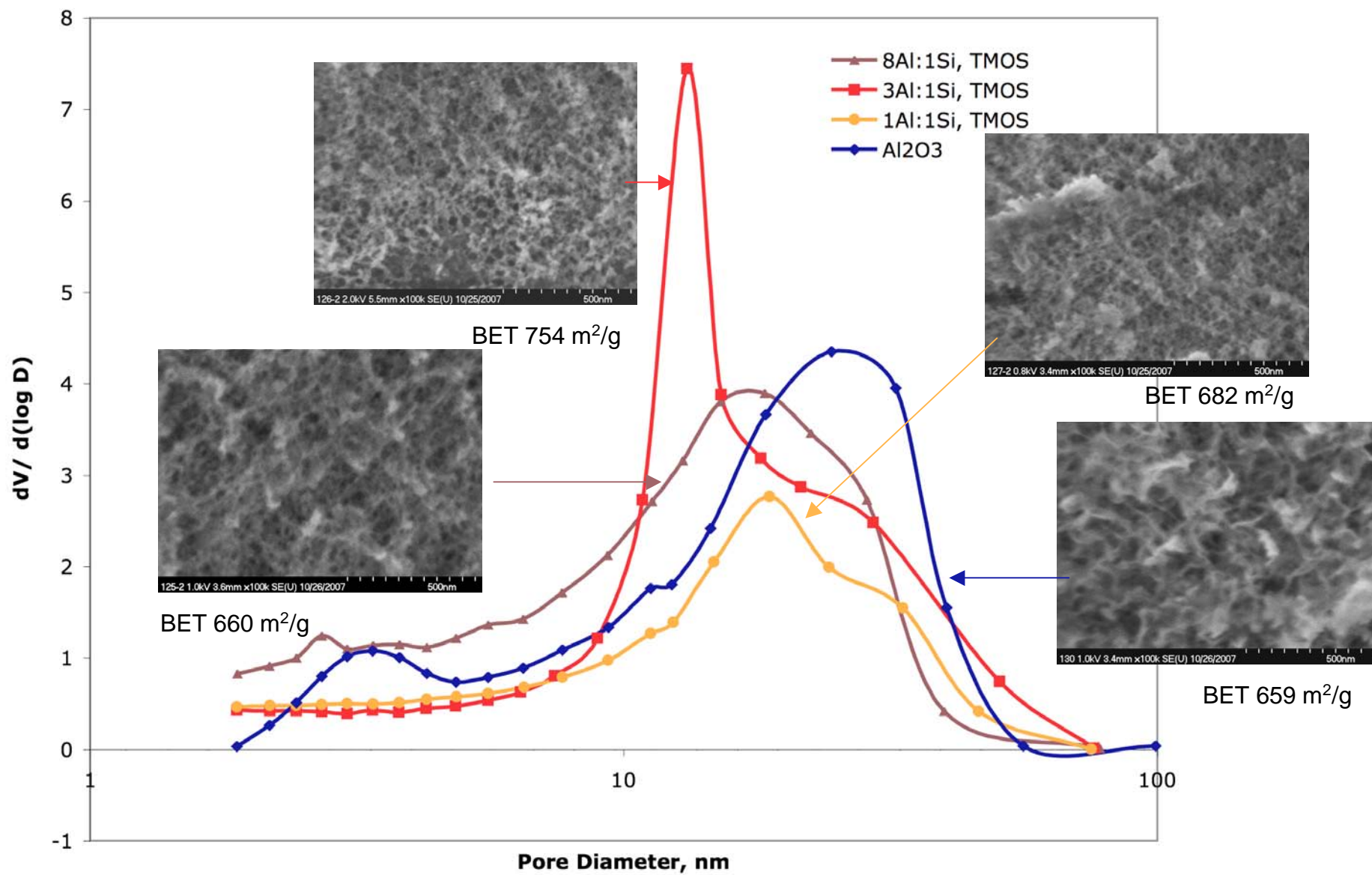
Al/Si ratio

water/ M

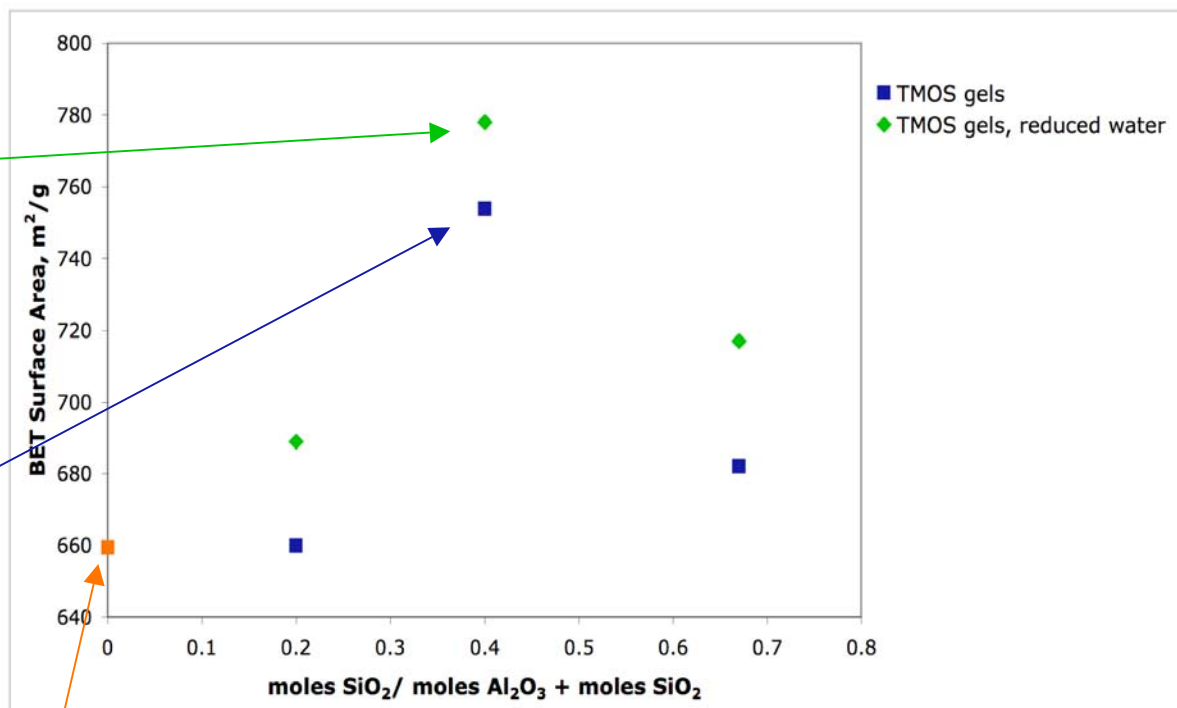
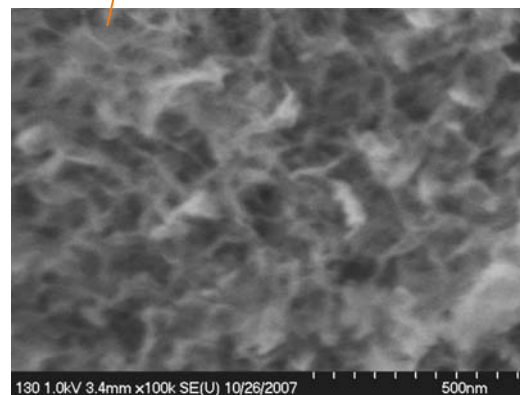
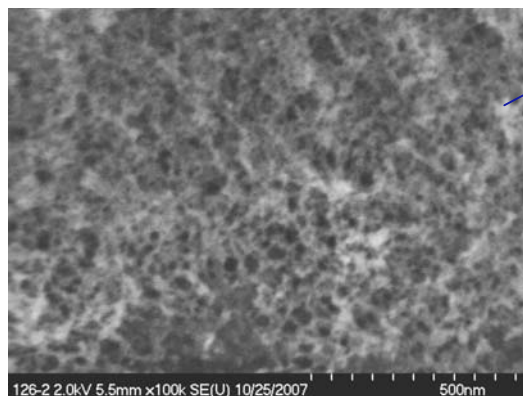
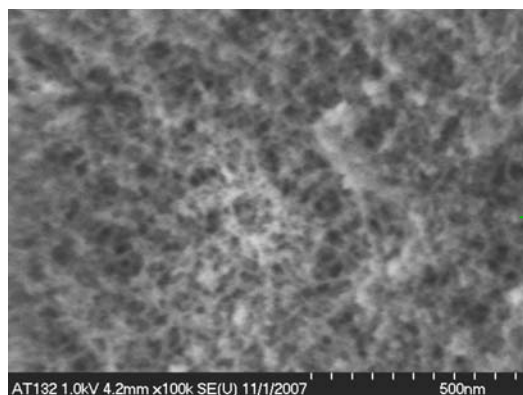
alcohol/ M

propylene oxide concentration

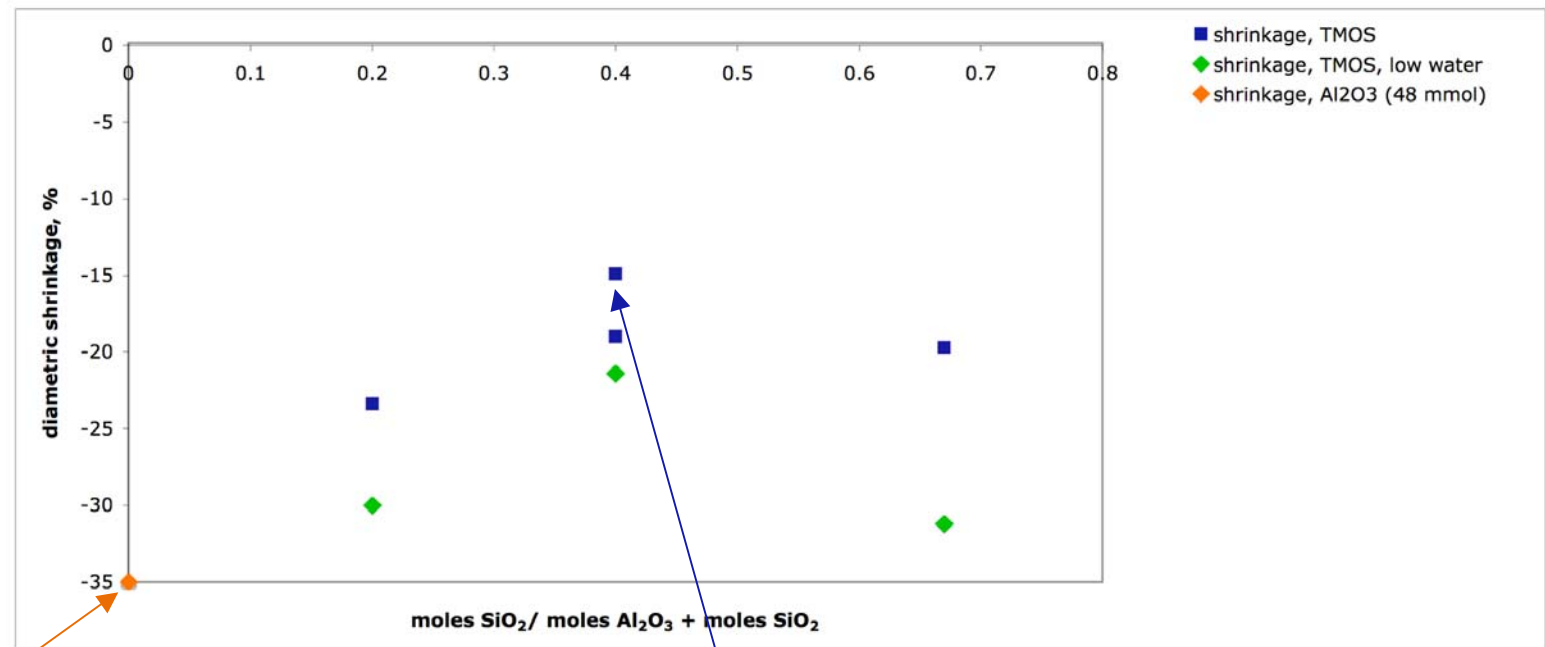
**Determine influence of processing parameters on shrinkage, gel structure (surface area, pore size and pore distribution, density) and pyrolysis behavior.**

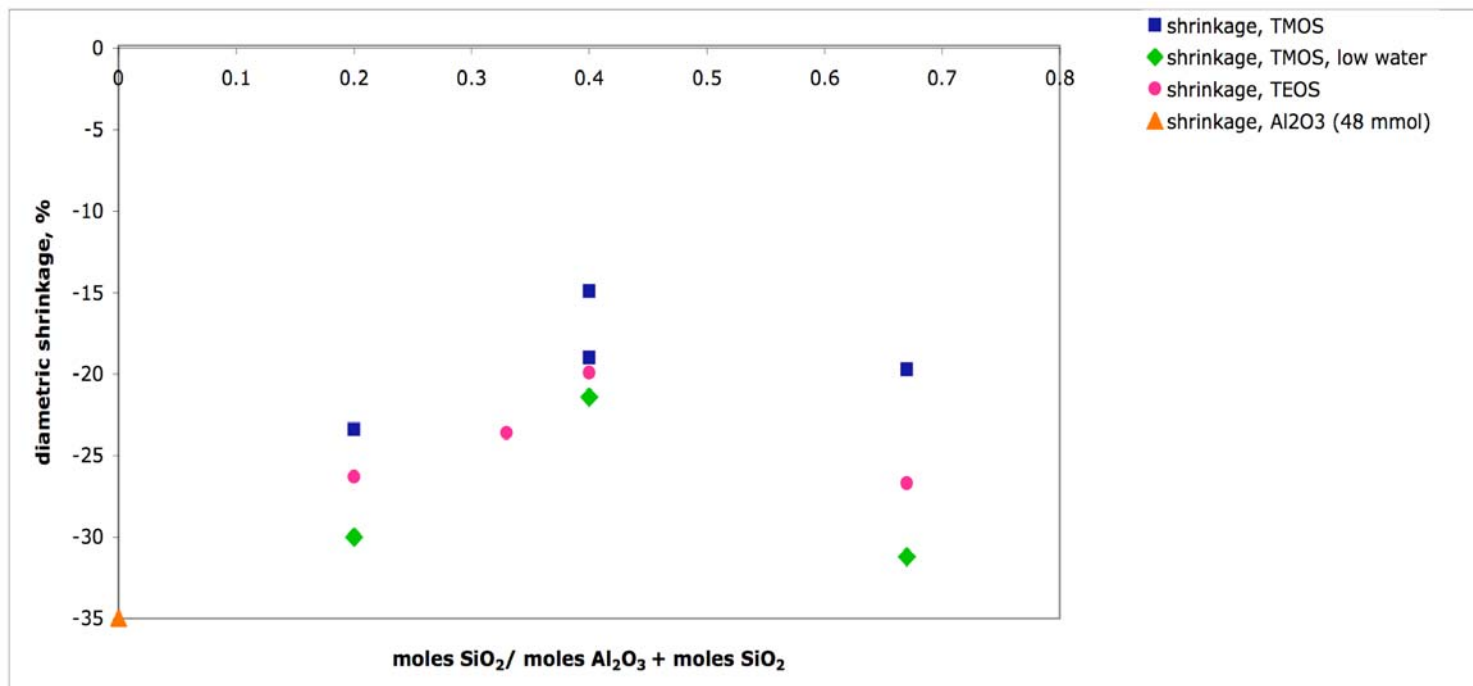




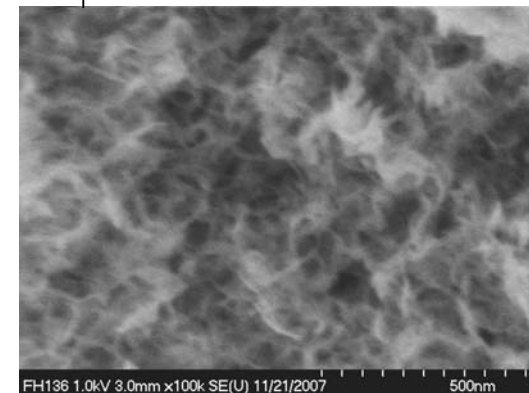
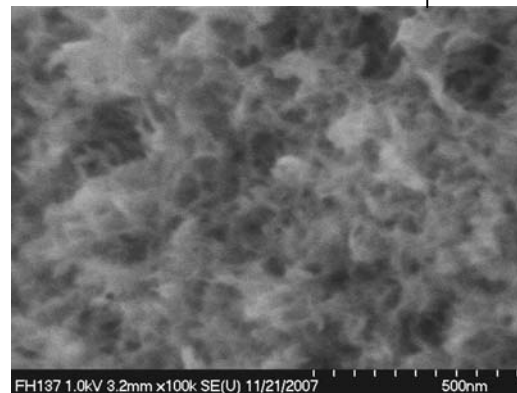
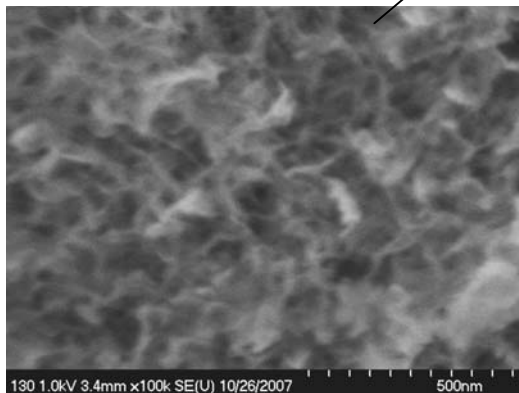
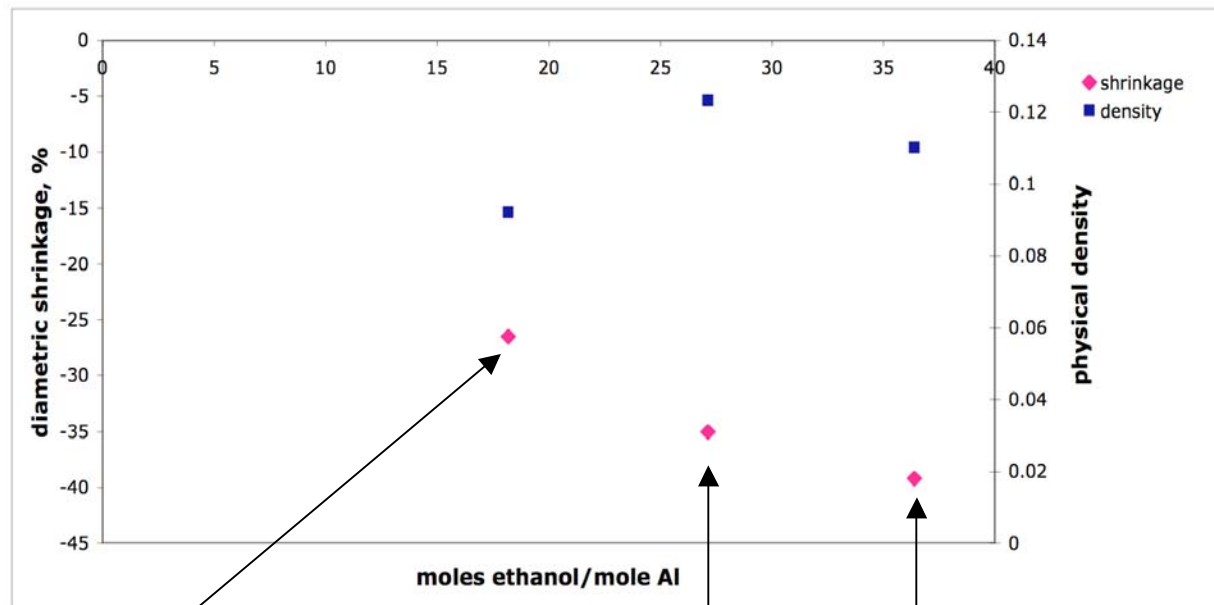


Shrinkage control is an important element in integrating aerogels with other materials.



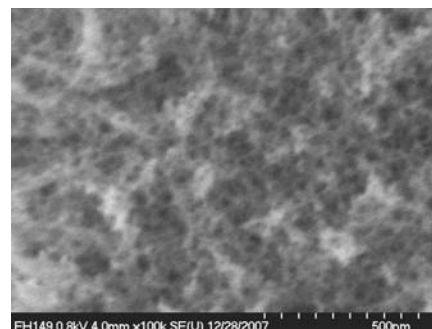


- Shrinkage varies with Al/Si composition as well as synthesis parameters.
- Al<sub>2</sub>O<sub>3</sub> gel has the greatest shrinkage, but is the most robust.
- TEOS provides a less toxic alternative to TMOS, but gels exhibit slightly greater shrinkage than TMOS-derived gels,
- Lowest shrinkage in this series obtained with 3Al: 1Si composition.

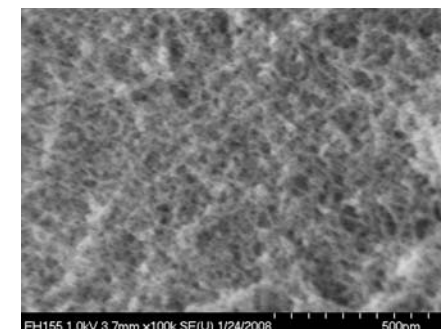


Note larger pores and coarser structure of  $\text{Al}_2\text{O}_3$  aerogels compared with mixed  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  gels

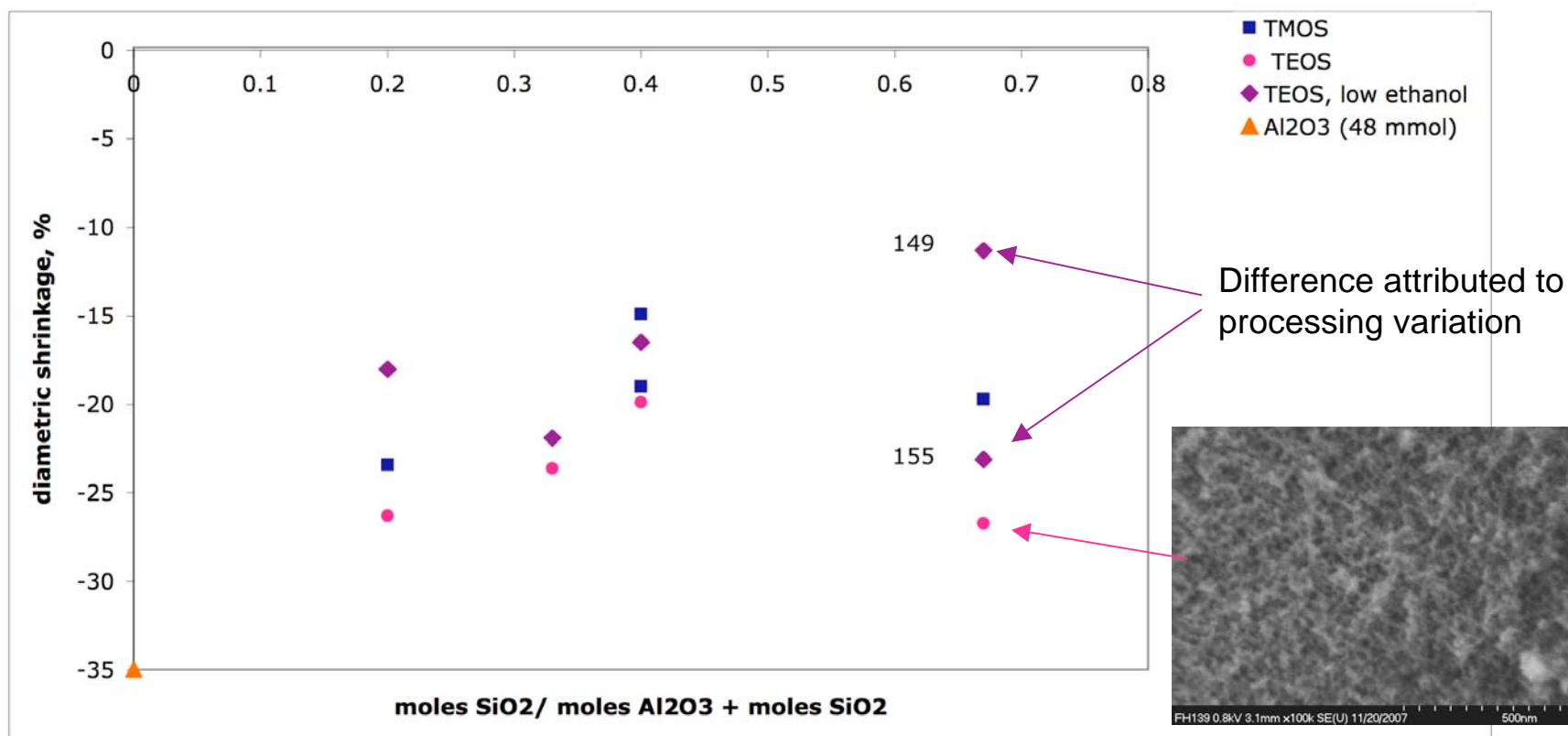
- 1:1 hydrogels show the lowest shrinkage (near net shape)
- Aerogels appear to have minimum shrinkage at 3:1 composition, with exception of 149 gel synthesized using a slightly modified technique.
- Lower ethanol might reduce shrinkage, but requires tighter process control.

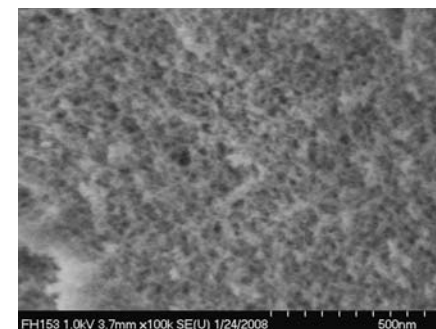
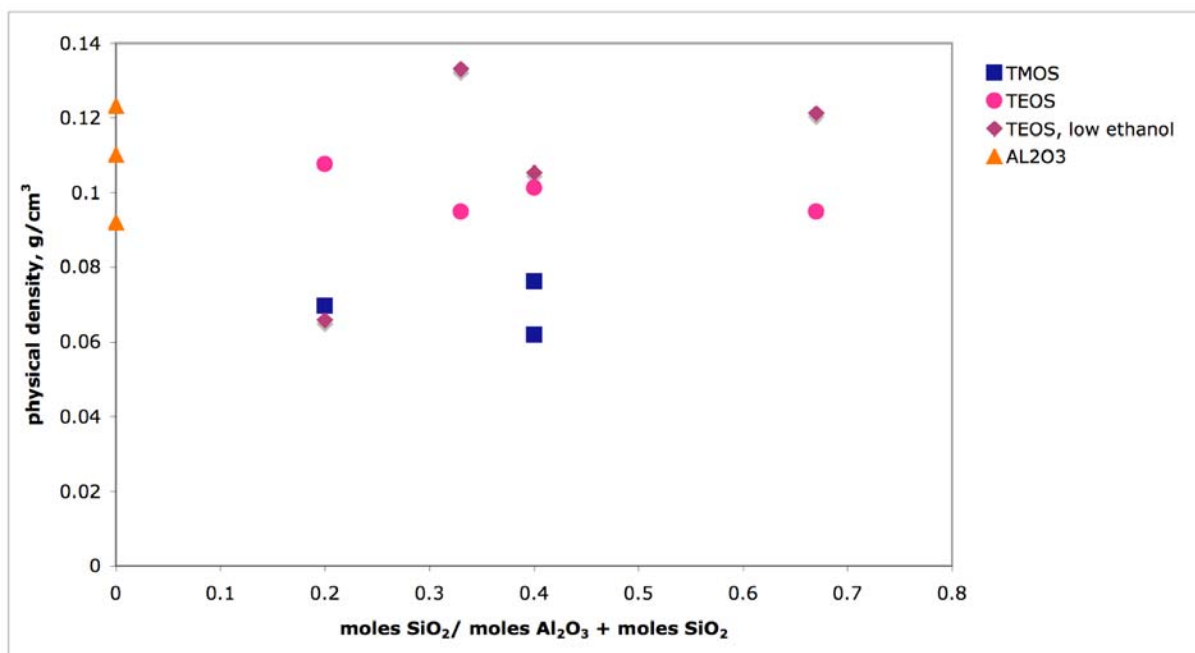


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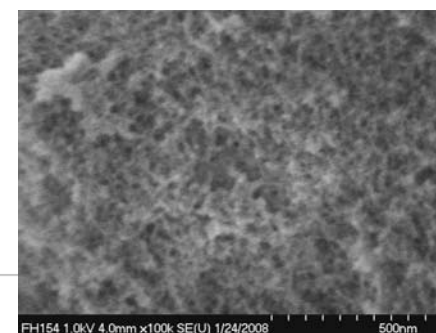


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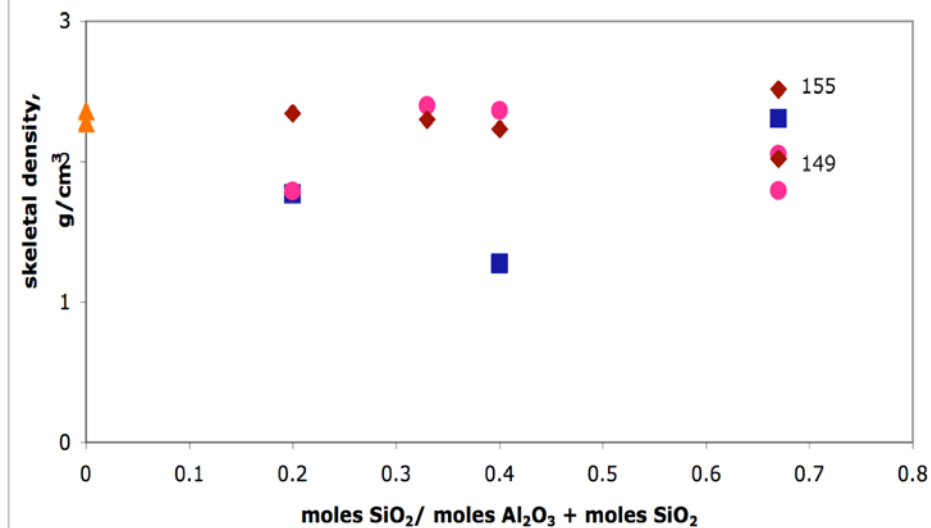




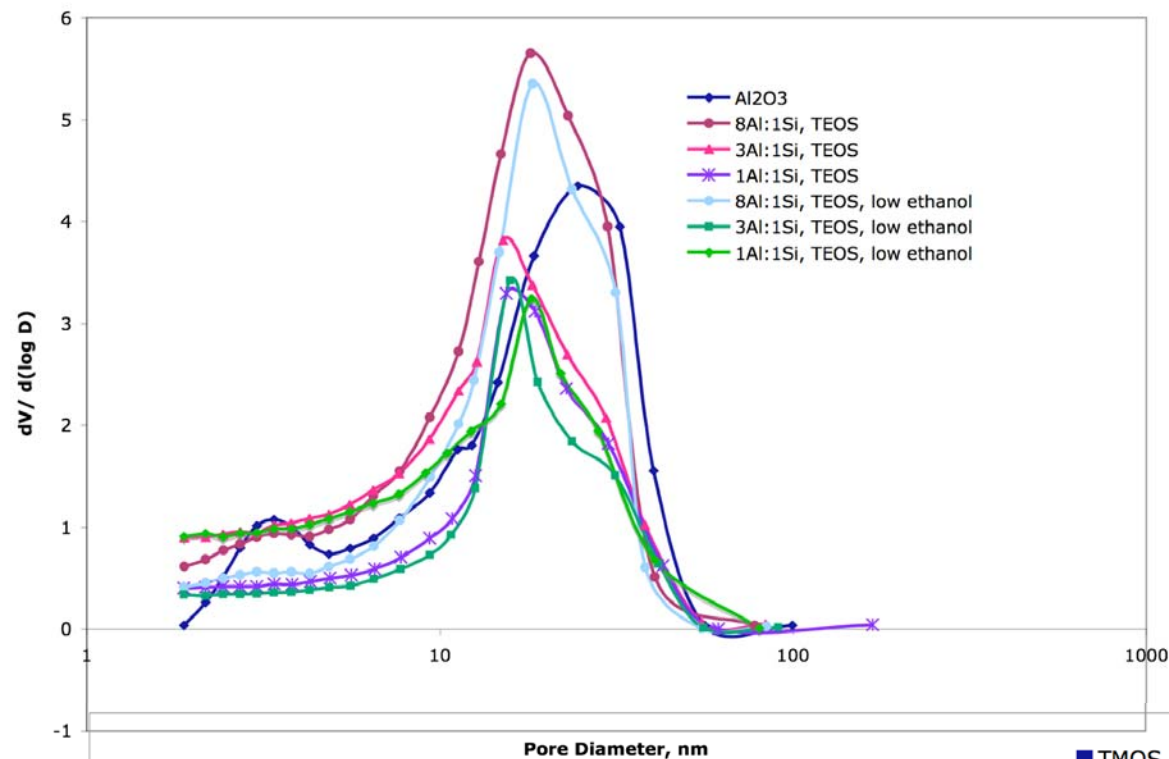
4Al:1Si, low ethanol



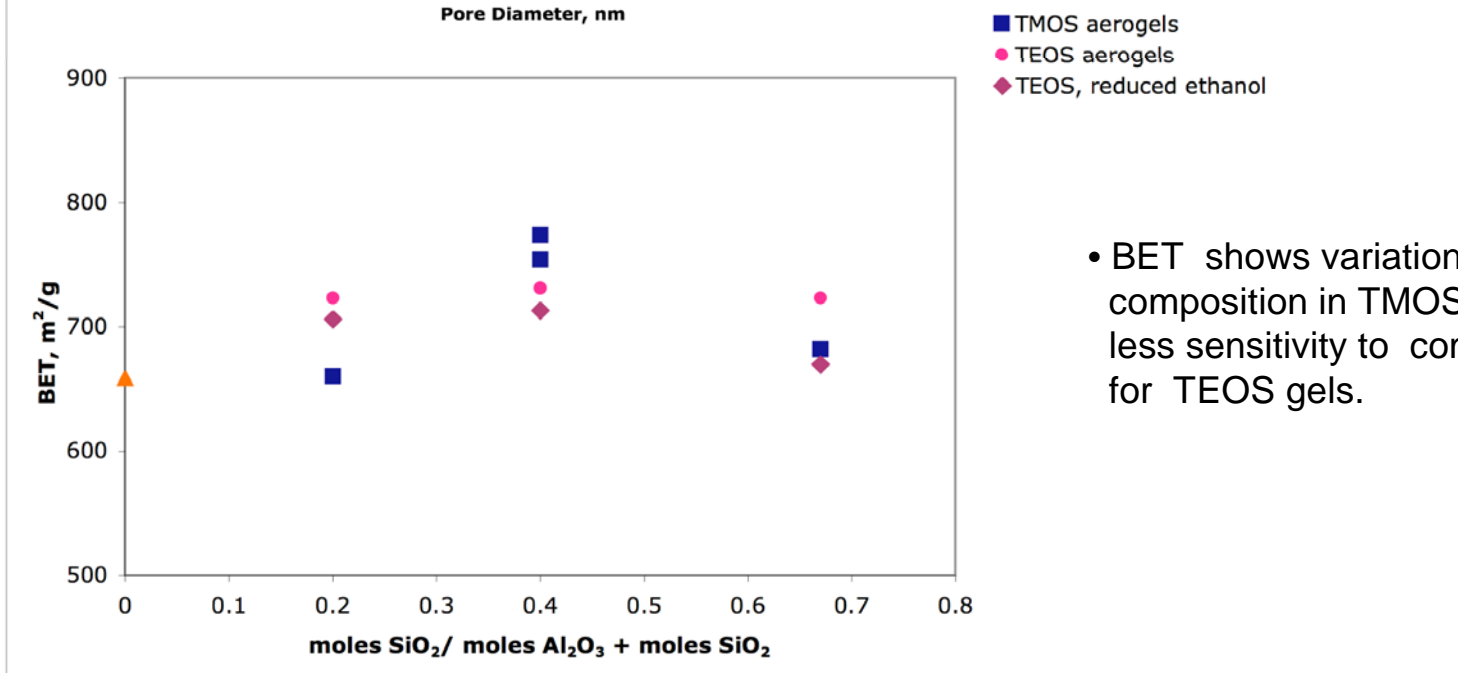
4Al:1Si



- porosity 94.5-96.4 %
- TMOS gels have lowest bulk density
- variation in physical density of low ethanol gels might reflect need to better control competing reactions during synthesis

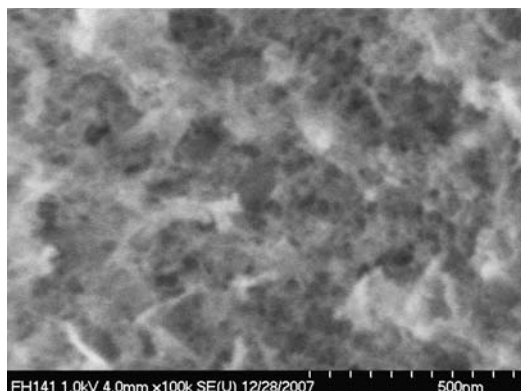


- Al<sub>2</sub>O<sub>3</sub> and 8Al:1Si gels exhibit larger pores and wider pore size distribution; Al<sub>2</sub>O<sub>3</sub> gel also contains 2.5-4.5 nm peak.
- Typical pore size smallest in 3:1 and 1:1 gels.
- Characterization of 4:1 gels in progress.

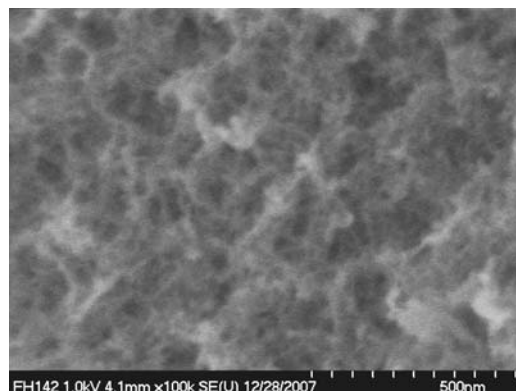


- BET shows variation with composition in TMOS aerogels; less sensitivity to composition for TEOS gels.

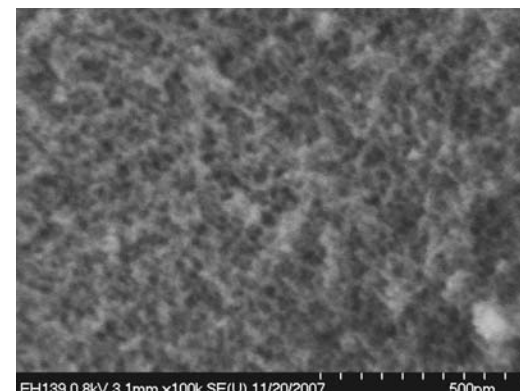




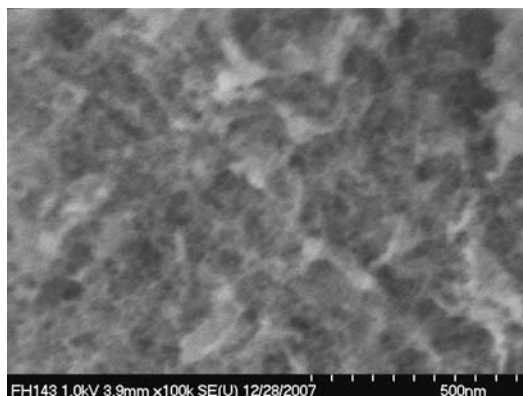
Al:Si 8.0:1.0 BET 723 m<sup>2</sup>/g



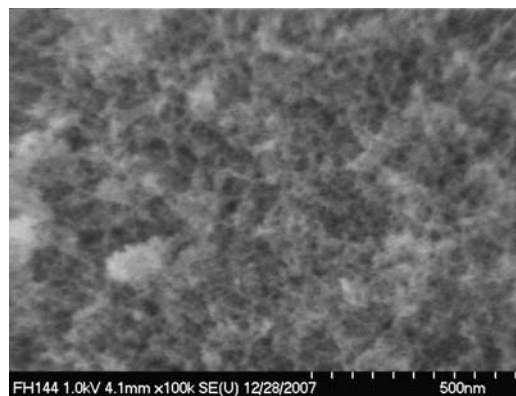
Al:Si 3.0:1.0 BET 731 m<sup>2</sup>/g



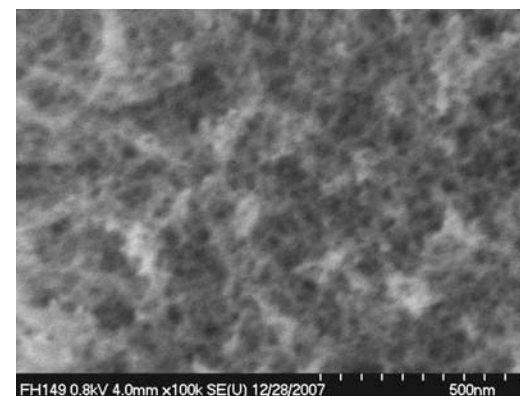
Al:Si 1.0:1.0 BET 723 m<sup>2</sup>/g



Al:Si 8.0:1.0 reduced ethanol  
BET 706 m<sup>2</sup>/g

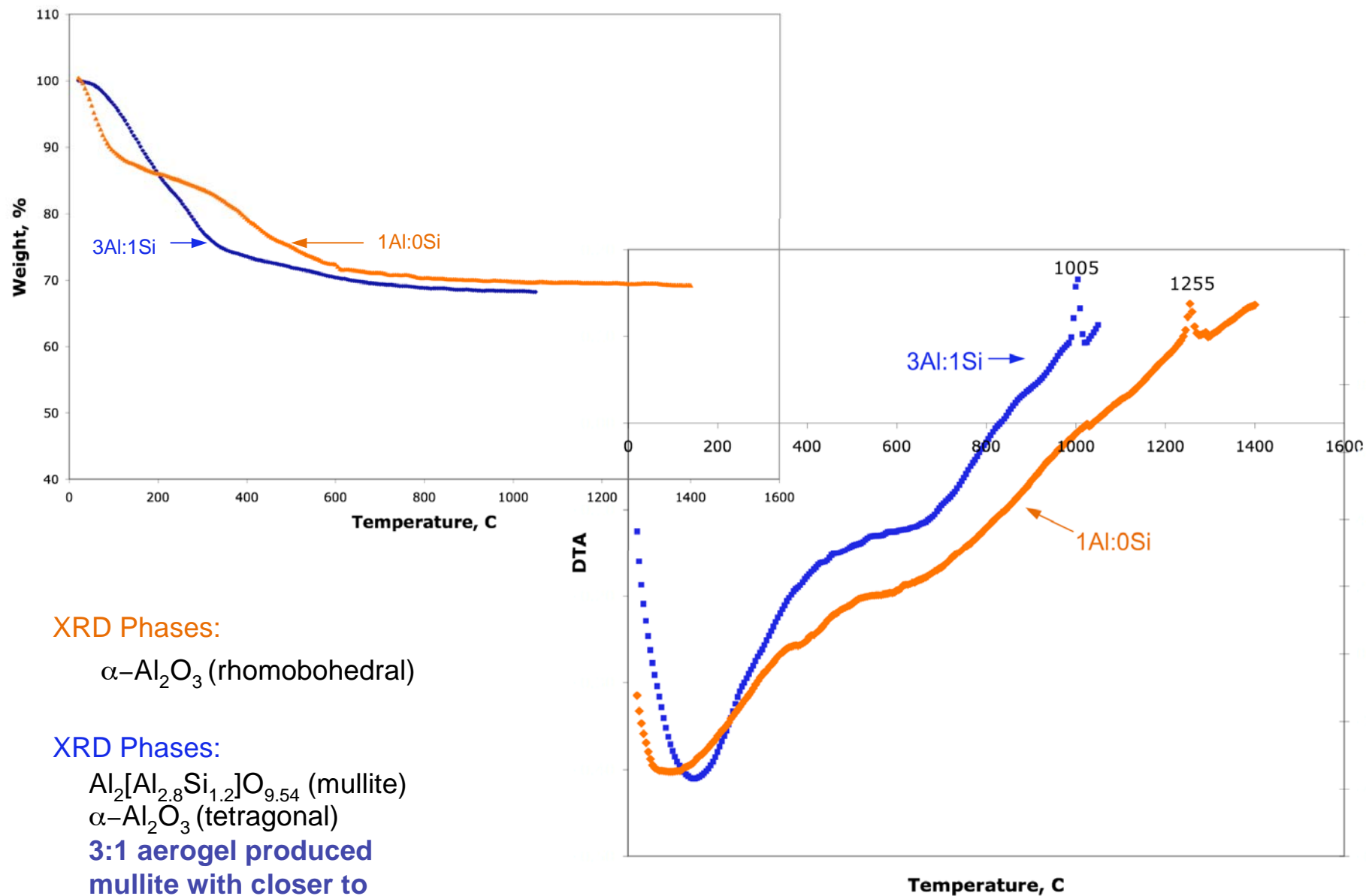


Al:Si 3.0:1.0 reduced ethanol  
BET 713 m<sup>2</sup>/g



Al:Si 3.0:1.0 reduced ethanol  
BET 670 m<sup>2</sup>/g





#### XRD Phases:

$\alpha$ - $\text{Al}_2\text{O}_3$  (rhombohedral)

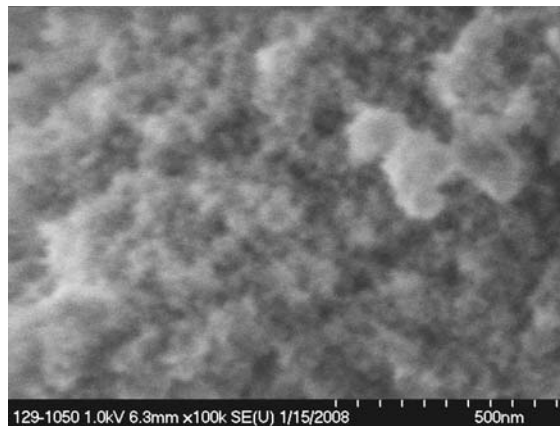
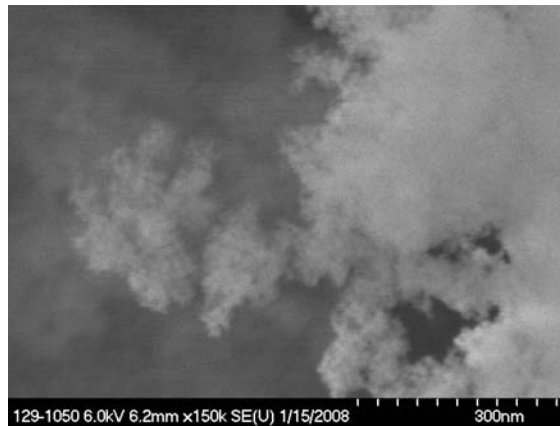
#### XRD Phases:

$\text{Al}_2[\text{Al}_{2.8}\text{Si}_{1.2}]\text{O}_{9.54}$  (mullite)

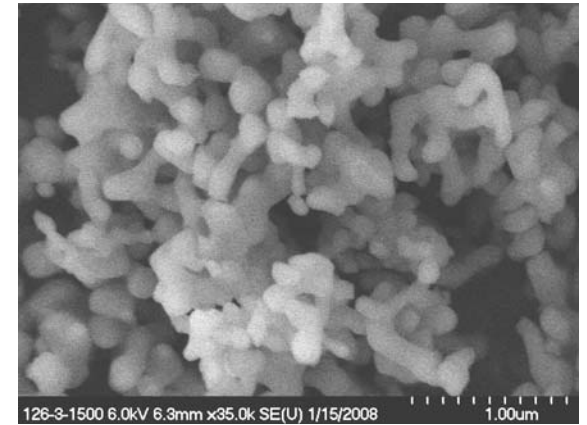
$\alpha$ - $\text{Al}_2\text{O}_3$  (tetragonal)

**3:1 aerogel produced  
mullite with closer to  
4:1 composition**

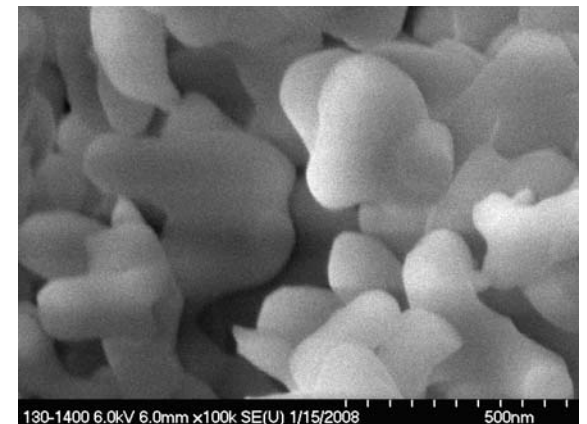
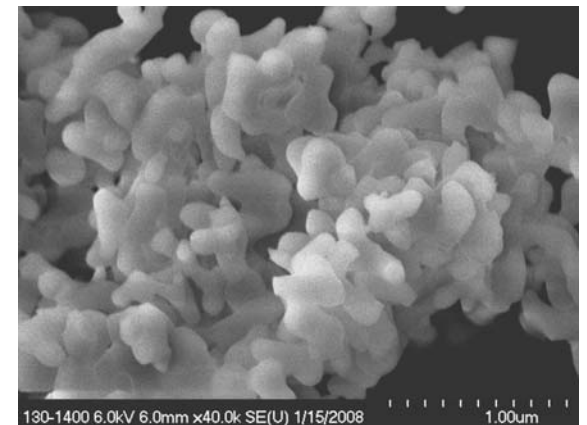
- Aerogel structure maintained after brief exposure to 1050 C in 3 Al: 1 Si gel
- Dense, crystalline structure obtained at 1400 C and above



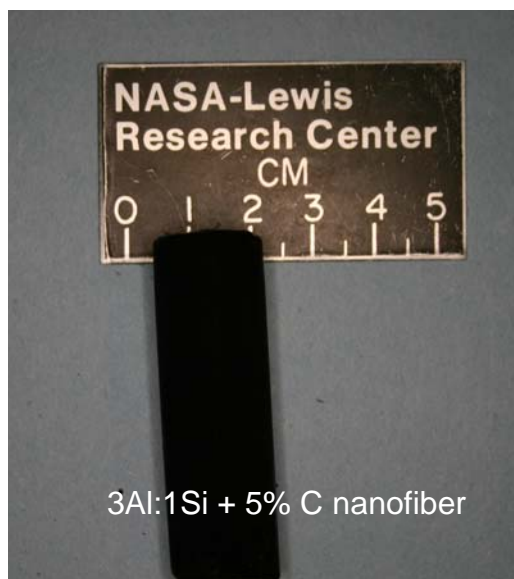
3Al:1Si, 1050C



3Al:1Si, 1500 C

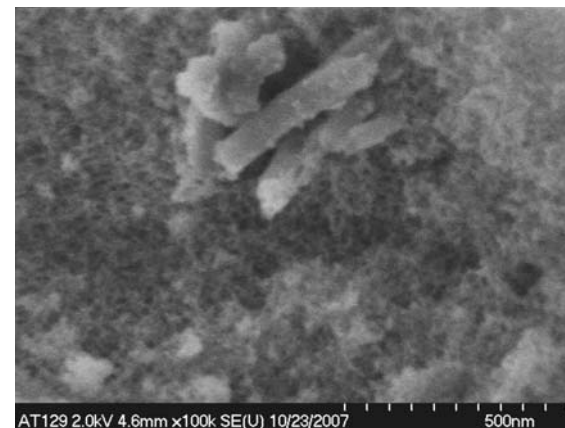
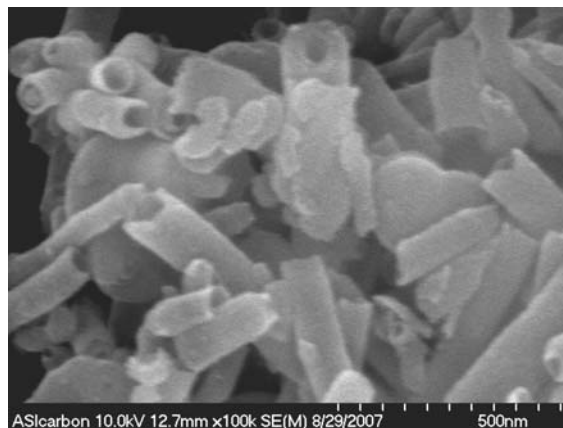


1Al:0Si, 1400 C



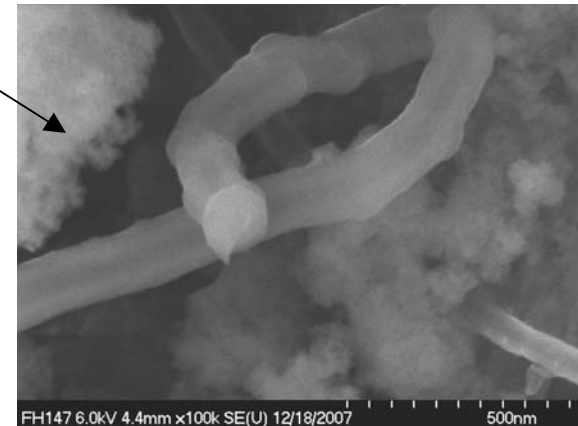
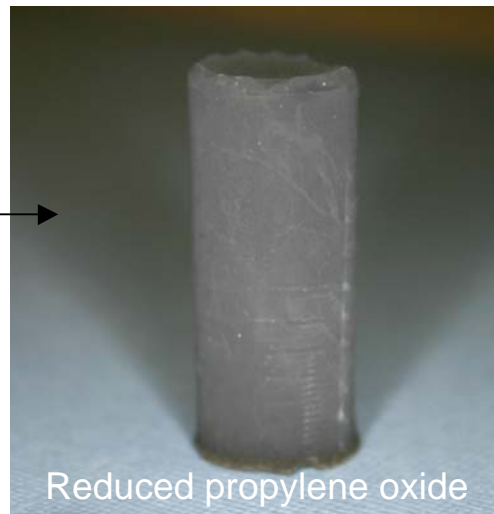
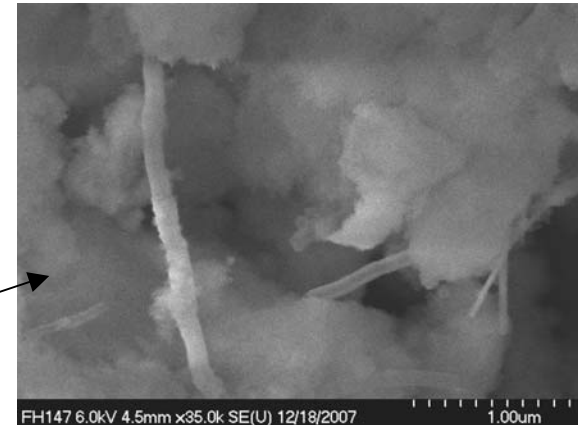
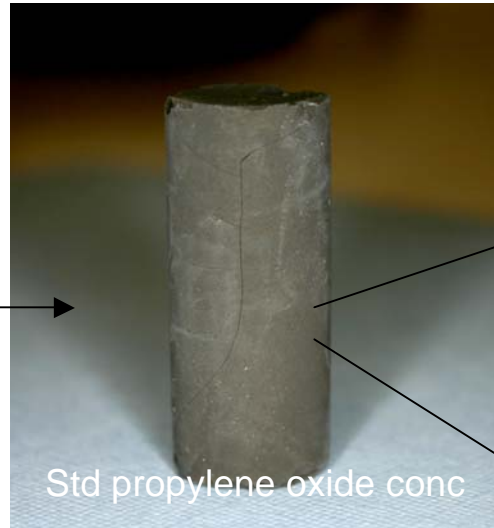
## Applied Science C nanofibers in $\text{Al}_2\text{O}_3\text{-SiO}_2$ aerogels

- Good dispersions attained with short fiber lengths in higher alcohol systems
- Radial splits developed at higher Al concentrations



## SiC Nanofiber (GRC) reinforced aerogels

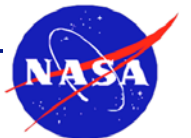
- Very rapid gelation occurs with addition of SiC nanofibers. Distinctly different from behavior with same weight percent of C nanofibers, suggesting some catalytic effect (requires further study)
- Reducing propylene oxide concentration delays gelation. In this case, gel time was sufficiently long that nanofibers settled, producing a gradient.
- Appropriate intermediate gel time should readily be attainable



5% SiC nanofiber in 3Al:1Si gel, low ethanol

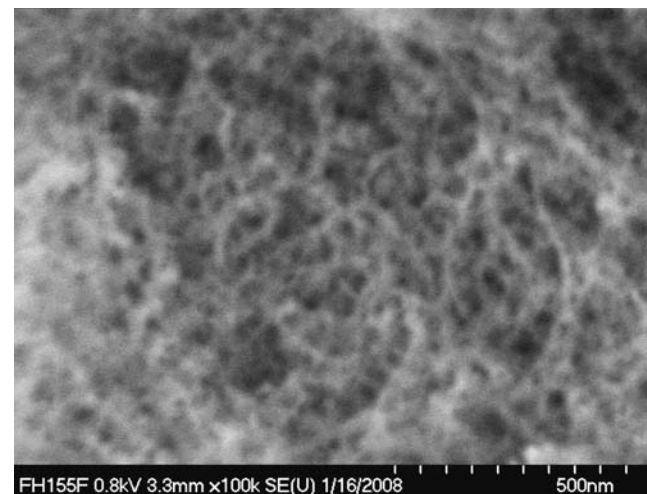
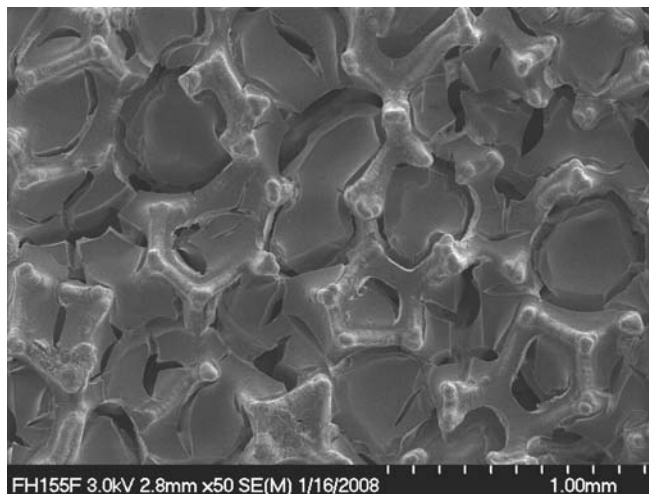
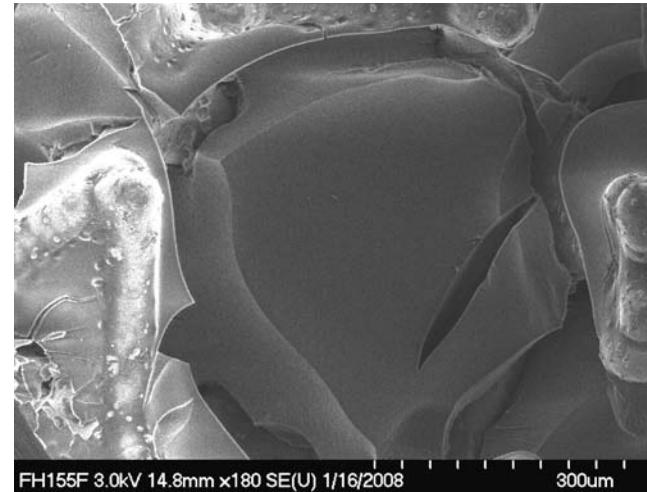
Alumina nanofiber reinforced aerogels:

Coming soon!



# Aerogel-Filled 100 ppi SiC Foam (HyperTherm)

1Al:1Si, reduced ethanol

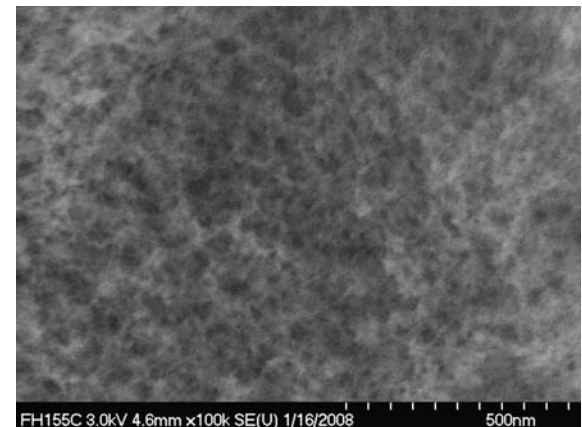
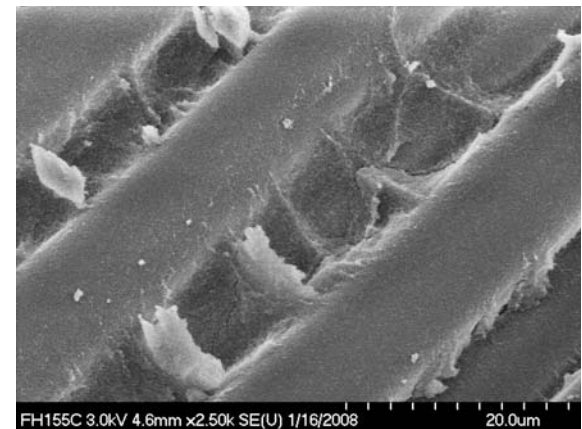






## Nextel 312 aerogel composite

- good infiltration of aerogel into fabric
- fabric remains flexible
- more successful in compositions with low syneresis
- needs development to avert delaminations



## Summary and Conclusions:

- Al-rich (all  $\text{Al}_2\text{O}_3$  and 8Al:1Si compositions) have larger pores and wide pore size distributions.
- Narrower, more uniform pore distributions can be attained with 4:1 and 3:1 compositions.
- TEOS can be substituted for more toxic TMOS, and provides more robust gels.
- Reducing ethanol concentration offers promise in reducing shrinkage, but may require tighter control of competing reactions in synthesis, and increases challenge in dispersing nanofibers.
- SiC nanofiber incorporation provides reduced shrinkage in 3:1 gel, but accelerates gelation. Gelation time can be controlled with appropriate propylene oxide concentration.
- 3:1 compositions maintained fractal structure at brief exposure to 1050 C.
- Al-rich compositions provide potential for highest temperature applications and are more robust.
- Si-rich compositions offer lower shrinkages, and thus are desirable for filling foams without pulling away from foam struts.

